

# A LASER-BASED SENSOR FOR AMBIENT DETECTION OF RDX AND TNT

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## ABSTRACT

We detect trace residues of RDX and TNT by surface photofragmentation - fragment detection in real time at ambient conditions. An infrared or visible laser generates signature, NO molecular fragments, and a second, low energy, ultraviolet laser facilitates their detection by resonance enhanced multiphoton ionization. We present the effects of pump laser wavelength, laser energy, delay timing between the pump and probe beams, and analyte concentration on signal intensity. Sensitivity analyses yield RDX and TNT detection limits in the low ng/cm<sup>2</sup>.

## 1. INTRODUCTION

The detection of energetic materials is a serious concern in the war on terror, either on the war front or in our homeland. With the widespread use of improvised explosive devices and the increased potential for homeland attack, a sensor that detects energetic materials that is robust, accurate, and easy to deploy would undoubtedly reduce the risk to warfighters and civilians. As a result, there has been much interest in developing such a sensor.

The vapor pressures of energetic materials hexahydro-1,3,5-hexanitro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT) are very low at ambient conditions. The following Clausius–Clapeyron equations express their concentration as a function of temperature:

$$\log P(RDX[ppb]) = \frac{-6473}{T[K]} + 22.50 \quad (1)$$

$$\log P(TNT[ppb]) = \frac{-5481}{T[K]} + 19.37, \quad (2)$$

where P is the pressure and T is the temperature (Dionne et al., 1986). At 298 K, the vapor pressure for RDX is 6 ppt and that for TNT is 9 ppb. The low number of airborne energetic particles created naturally under ambient conditions challenges the sensor's sensitivity requirement.

Humans teamed with canines or other animals can

detect energetic materials by means of the animal's sensitive, olfactory receptors. Unfortunately, the teams require training, and fatigue from either team member, false positives, or low sensitivity for some compounds hinders their effectiveness for trace energetic material detection. Lasers are gaining widespread use outside the laboratory for their ability to accurately detect spectroscopically low concentrations of energetic materials in real time at ambient conditions. Two laser techniques are laser induced breakdown spectroscopy (LIBS) and laser photofragmentation (PF) - fragment detection (FD).

LIBS uses high-powered, focused lasers to create a plasma at the site where the laser interacts with the material, completely breaking down a complex energetic material into its constituent elements (Munson et al., 2005, 2007, and references therein). Commonly, LIBS employs a Nd-YAG laser with a primary output wavelength of 1064 nm. Sometimes, the Nd-YAG output is frequency doubled, tripled, and even quadrupled because of the lower amount of laser pulse power needed to create a plasma at shorter wavelengths. The material is identified by examining the elemental spectra looking for intensity ratios of two elements, elevation of certain elements above ambient conditions, the presence of strange elements, etc. (Munson et al., 2005). This method of identification can be a problem for a large number of energetic materials due to the common elements found in their composition; namely carbon, nitrogen, and oxygen.

PF/FD techniques use one or multiple lasers to identify the energetic materials (Lemire et al., 1993; Simeonsson and Sausa, 1998; Heflinger et al., 2002; Cabalo and Sausa, 2005, and references therein). One laser tuned to a specific wavelength both photofragments the target molecule and facilitates the detection of characteristic fragments by resonance enhanced multiphoton ionization (REMPI), laser induced fluorescence (LIF), or both. Alternatively, in a two-laser setup, one laser photofragments the target molecule and a second laser, time-delayed from the first laser, probes the photofragment. As opposed to LIBS, photofragmentation causes the complex molecule to break down into larger fragments or signature molecular groups. These molecular groups would not commonly be found in large quantities under ambient conditions, indicating the presence of the energetic material.

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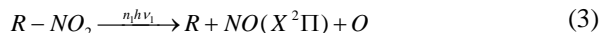
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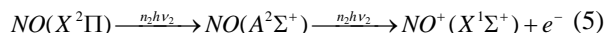
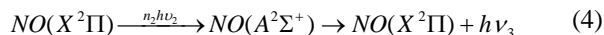
In this paper, we present our results on the detection of trace RDX and TNT at ambient conditions using a surface PF/FD technique. An infrared or visible laser generates characteristic NO fragments from the target material and an ultraviolet laser tuned to near 226 nm facilitates their detection by REMPI. We report the effects of analyte concentration, laser energy, and time-delay between lasers on signal intensity, and determine detection limits for both RDX and TNT.

## 2. APPROACH

Figure 1 illustrates the PF/FD technique for energetic materials. Many energetic molecules have NO<sub>2</sub> groups, as shown in figure 2 for RDX and TNT, that are weakly bonded to their skeletal structure. Infrared, visible, or ultraviolet laser radiation ruptures these bonds to form excited or ground state NO<sub>2</sub> molecules. Oftentimes, the excited, displaced NO<sub>2</sub> molecules predissociate and NO molecules are readily created:



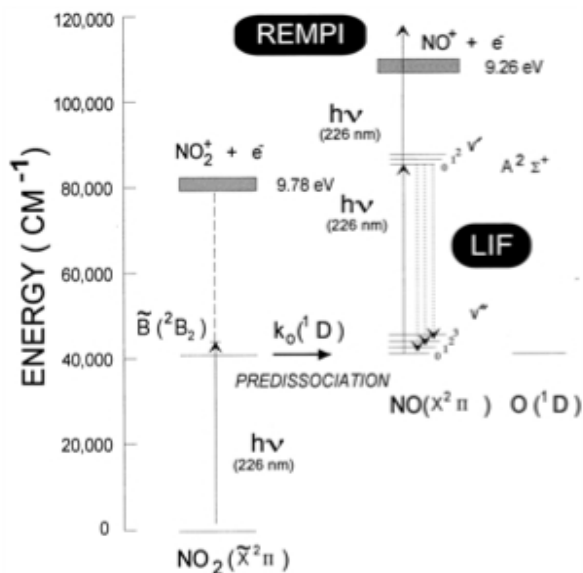
NO is then detected by its prompt emission if formed electronically excited, or by LIF, REMPI, or both, if formed in its ground electronic state. The LIF and REMPI processes are represented by the following equations:



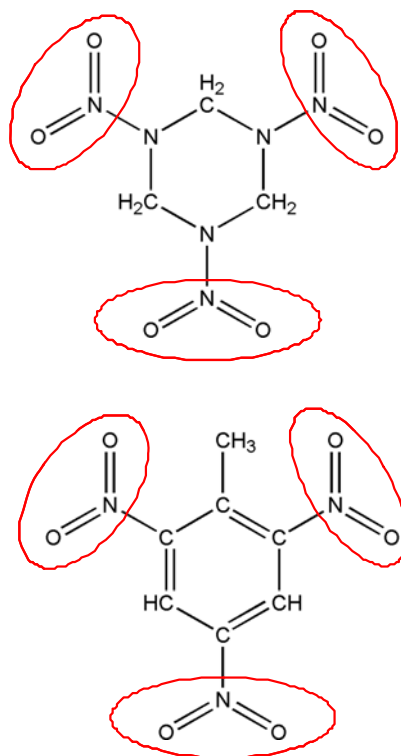
The photofragmentation and detection processes depicted in the above expressions are extremely fast, typically in the fsec to msec- timescale.

LIF is widely used to detect airborne NO because of its ease of setup and sensitivity. LIF also offers the ability to make measurements in real time that allow for calculations of quantities like temperature and concentration (Andresen, 2001). It has been widely used to detect NO in a number of places including exhaled human air (Mitscherling et al., 2007), high altitude (Sandholm et al., 1997), and flames (Venizelos and Sausa, 1998).

One significant challenge when trying to use LIF to detect energetic materials under ambient conditions is collisional quenching. Collisional quenching at atmospheric pressure reduces the radiative lifetime of



**Figure 1 -- An energy diagram of PF / FD for NO detection from an NO<sub>2</sub> fragment. The energies required for both REMPI and LIF are shown.**



**Figure 2- Structural Diagram of RDX (top) and TNT (bottom). The circled NO<sub>2</sub> groups are the signature molecular fragments to be detected using PF/FD.**

NO making it more difficult to detect. An excited NO fragment is more likely to transfer its energy to a neighboring molecule without emitting a photon at atmospheric pressure as opposed emitting one at lower pressures. REMPI mitigates this problem to a large extent because the ionization process is much faster than the collision quenching process.

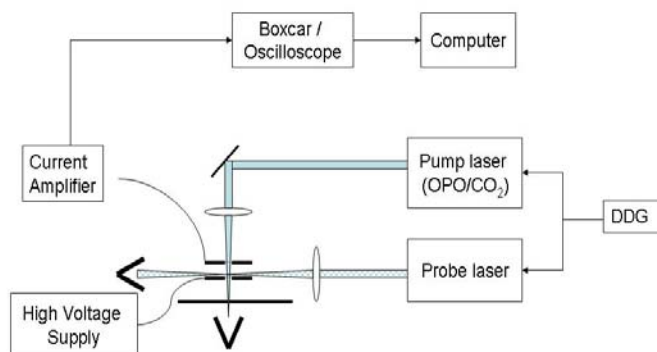
In the REMPI technique, a laser selectively creates ions of interest in an electric field between two plates. The plates capture almost all of the charged particles, making for a more effective detection of small amounts of NO than LIF. REMPI has been used to detect NO in a number of experiments. It was used to detect concentrations of NO in a NO/NO<sub>2</sub> gas mixture (Pastel and Sausa, 2000). Most importantly for this research, previous work shows that we can detect TNT easily using REMPI at atmospheric pressure (Swayambunathan et al., 1999).

### 3. EXPERIMENTAL SETUP

We use a two-laser, pump-probe system to detect energetic materials on quartz substrates. A schematic of the experimental setup is seen in Figure 3. A continuous, infrared laser (CO<sub>2</sub> Synrad Series 48-2-28 (W)) or visible laser (Continuum Sunlite EX OPO pumped by a Continuum Powerlite® Precision II Nd:YAG laser) generates airborne energetic molecules or the characteristic NO fragments, and an ultraviolet laser (frequency doubled, Lumonics Hyperdye 300 laser, pumped by a Continuum Surelite II Nd:YAG laser) facilitates their detection by REMPI. The laser wavelengths are approximately 9.6 to 11.6  $\mu\text{m}$ , 455, 470, 500, and 550 nm, and  $\sim 227$  nm, and their respective energy is up to 2 J, up to 35 mJ, and  $\sim 50$   $\mu\text{J}$ .

The probe laser beam passes through either a germanium lens with a focal length of about 38 mm or quartz lens with a focal length of 75, 200, or 300 mm that focuses the beam near the substrate's surface containing the energetic material. The surface is near the focal length of the lens but not at the focal point; 0.6 mm for the infrared lens and 60, 163, and 261 mm for the 75, 200, and 300-mm quartz lenses, respectively. If the surface is too close to the focal point, the pump laser beam will either etch the surface or create a plasma, thus producing false REMPI signals. Our infrared laser fluence is  $\sim 0.4$  J/cm<sup>2</sup> and our visible laser fluence ranges from 0.6 to 1.4 J/cm<sup>2</sup>.

The REMPI probe is fabricated in-house. It contains two metal plates about 1.3 cm by 2 cm in size with two, 3.2-mm holes in the center that allow the pump beam to pass through and strike the surface. The plates are 4 mm apart from each other, and the lower plate is 1 mm from the substrate's surface. The average



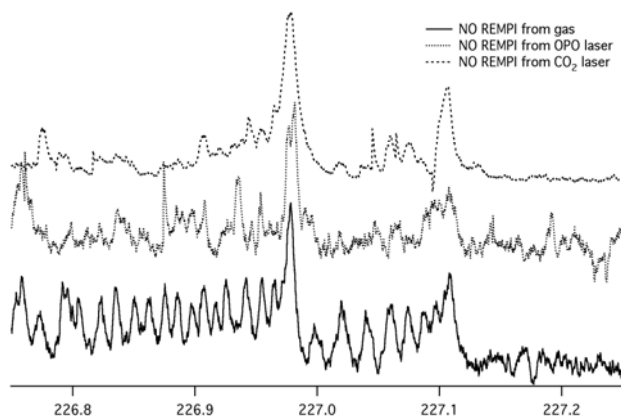
**Figure 3 – Diagram of the experimental setup.**

electric field is 250 V/mm for a 1000-V bias between the plates. A current amplifier (Keithley 427, gain  $10^6$ - $10^7$  V/A, time constant 0.01 ms) amplifies the signal, whose output is fed to a 125-MHz oscilloscope (LeCroy 9400) for display. A personal computer records the signals from a boxcar averager (Stanford Research Systems, SR250). We use a digital delay generator (Stanford Research Systems, DG535) to control the pulse length of the infrared lasers, as well as the time delay between the pump and probe lasers.

We prepare thin films of TNT and RDX by coating circular quartz plates with 1 ml of dilute solutions of the target compound in methanol and then evaporating the solvent with a hotplate. We mount the substrate on a computer-controlled, XYZ stage and record the ionization signal with the pump beam on, while we simultaneously move the substrate at a rate of  $\sim 7$  mm/sec and scan the probe laser at a rate of 0.0025 nm/s over the region of 226.75 to 227.25 nm. We determine the technique's sensitivity by recording the REMPI response of TNT and RDX films prepared from serial dilution of  $\sim 0.17$  g/ml of TNT/methanol or RDX/methanol stock solution. The REMPI response for a given sample concentration is the integral of the area underneath the curve for each spectrum.

### 4. RESULTS AND DISCUSSION

Figure 4 shows REMPI spectra of NO from TNT and NO. We employ infrared, laser radiation or 450-nm radiation to vaporize/photolyze the target material and ultraviolet laser radiation to selectively excite the characteristic NO fragment. The infrared laser power is 200 mW, whereas the visible and ultraviolet laser energy is about 18 mJ and 50  $\mu\text{J}$ , respectively. We also show a spectrum of NO in a gas cell at ambient conditions for comparison purposes. The prominent spectral features of the energetic material are similar to those of NO, and are attributed to NO rotational lines of the  $A^2\Sigma^+ - X^2\Pi$  (0,0)

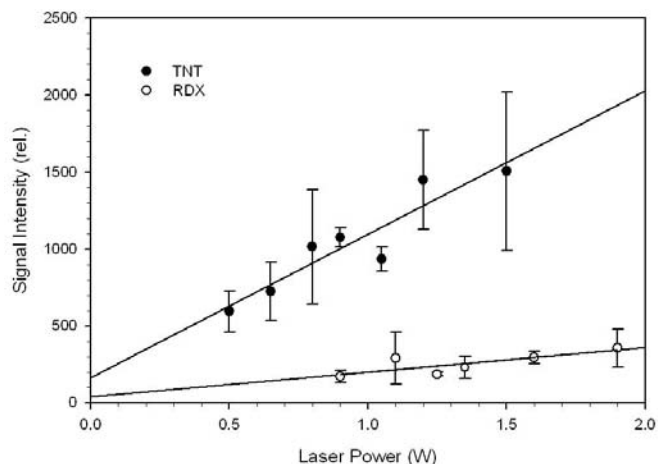


**Figure 4 – REMPI signal from NO from a gas cell, from the sample using an infrared laser, and from the sample using a visible laser.**

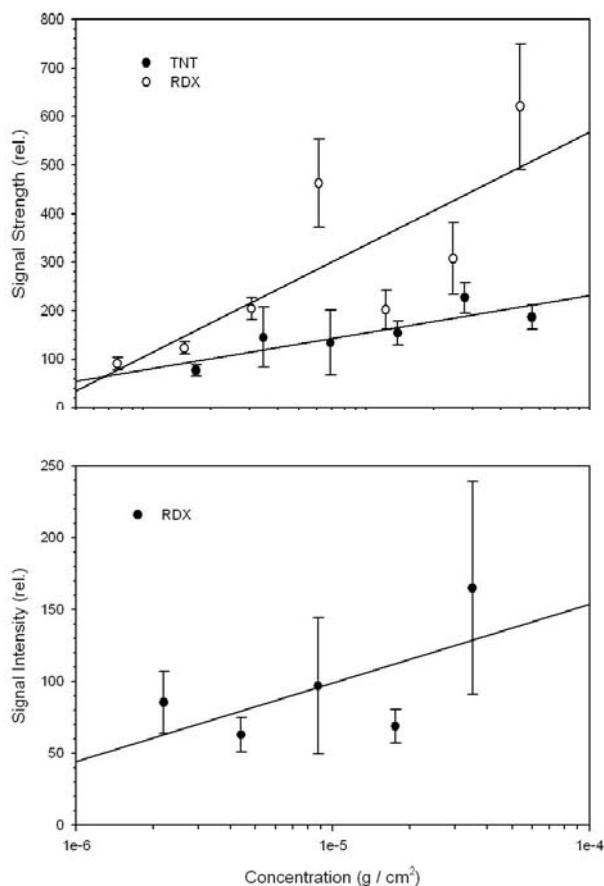
band. The visible laser spectrum is easily reproduced compared to the infrared laser spectrum, which was more difficult to obtain. Pump laser wavelengths of 470, 500, and 550 nm yield similar spectra that show the main NO features.

Figure 5 shows the NO signal dependence on infrared laser power for TNT and RDX. The pulse duration is 500 microseconds. The signal strength increases linearly with laser power for both compounds, but RDX's response is almost a factor of 10 more than TNT's response at 1 W. Also, an increase in laser fluence per unit time increases the signal intensity, as expected. We obtain similar results with 455-nm laser radiation up to about 20 mJ. Under our experimental conditions, our laser power densities are insufficient to either etch the quartz or generate a plasma at the quartz's surface.

Figure 6 shows the NO signal dependence on TNT and RDX concentration using the infrared pump laser (top) and visible laser (bottom). The time delay between the pump and probe laser is 1 ms. We find that the signal intensity does not change when we vary the pump-probe delay between 1 and 10 ms. As shown in figure 3, the RDX and TNT signals are linear over a wide range of concentrations. Also, the response signals of RDX are greater than those of TNT. Cabalo and Sausa report a similar trend using a similar setup, but with a 248-nm pump laser (Cabalo and Sausa, 2005). They attribute RDX's higher sensitivity compared to that of TNT to the fact that the nitrogen-nitrogen bond found in RDX is weaker than the carbon-nitrogen bond found in TNT. More energy from the laser is needed to overcome this bond in the TNT molecule, resulting in a lower level of detection for TNT than RDX. They also point out that TNT has several alternative decomposition pathways that compete with R—NO<sub>2</sub> bond scission such as CH<sub>3</sub> oxidation to form anthranil, nitro-nitrite isomerization, and catalysis. These pathways also decrease the initial



**Figure 5 - Signal strength vs. laser power. As the laser energy increases, the signal strength from the REMPI probes increases, indicating better detection**



**Figure 6 – Concentration analysis graph for the CO<sub>2</sub> laser (top) and the OPO laser (bottom).**

production of NO<sub>2</sub> and contribute to TNT's lower sensitivity relative to RDX. A sensitivity analysis of our data that utilizes knowledge of effected area of the energetic material yields RDX and TNT detection limits in the order of ng/cm<sup>2</sup>.

## CONCLUSION

The surface PF/FD technique exhibits great potential for detecting residues of RDX and TNT at ambient conditions in real time because of its high sensitivity and selectivity. The probe laser generates copious, signature NO fragments, which are detected by REMPI using a probe laser. This technique is not restricted to TNT and RDX, and has the potential to be extended to other energetic materials.

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